

REMARKS

Amendments

Claims 1-8 and 10-12 are amended to use language in accordance with conventional US practice. Claim 9 is cancelled. Claim 11 is also amended to be a method claim, rather than a use claim. See, e.g., page 1, lines 9-11. Furthermore, claim 12 is amended to recite additional structure of the display. See, e.g., page 22, lines 11-16.

New claims 13-23 are directed to further aspects of applicants' claimed invention and are supported throughout the disclosure. See, e.g., page 6, lines 20-26, page 7, lines 4-25, and page 11, lines 29-37.

Requested Article

Pursuant to the Examiner's request, enclosed is a copy of the Kirsch et al. article cited in the Information Disclosure Statement filed November 23, 2005.

Claims 9 and 11

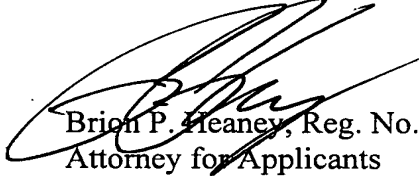
As noted above, claim 9 is cancelled and use claim 11 is converted into a method claim. Withdrawal of the objection and rejection of claims 9 and 11 is respectfully requested.

Obviousness-Type Double Patenting

Claims 1-12 are rejected on grounds of obviousness-type double patenting in view of claims 1-16 of US 7,189,440. For purposes of obtaining an early allowance of the instant application, applicants are filing herewith a Terminal Disclaimer with respect to US 7,189,440. Submission of this Terminal Disclaimer is not to be construed as acquiescence to any ground of rejection. Withdrawal of the rejection and allowance of the instant application is respectfully requested.

The Commissioner is hereby authorized to charge any fees associated with this response or credit any overpayment to Deposit Account No. 13-3402.

Respectfully submitted,



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Novel Polar Liquid Crystals with Very Low Birefringence Based on *trans*-1,3-Dioxane Building Blocks**

By Peer Kirsch* and Eike Poetsch

For the next generation of multimedia liquid-crystal displays (LCD) with video-compatible short response times and low power consumption there is a strong demand for new liquid-crystalline materials with high dielectric anisotropy ($\Delta\epsilon$), low birefringence (Δn), favorable mesogenic properties, low rotational viscosity (γ_1), and high voltage holding ratio (VHR).^[1] Presently, the sum of these desired properties can be only partially approached, either by using compounds with highly fluorinated aromatic substructures^[2] or by use of cyanobicyclohexane^[3a] or cyanophenylcyclohexane derivatives^[3b].

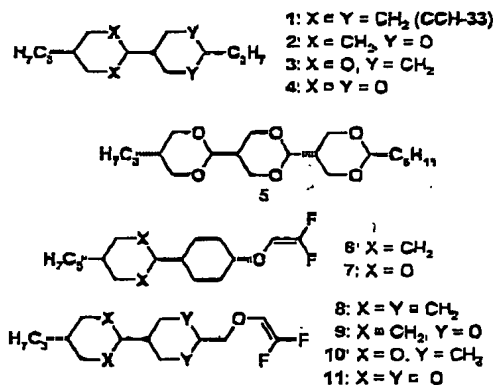
The two major disadvantages of most of the low γ_1 fluoroaromatic liquid crystals currently in use for active matrix displays (AMD) are their low clearing temperatures (below -50°C for di- and trifluorinated two-ring compounds) and their relatively high birefringence ($\Delta n > 0.075$). On the other hand, the main problems of all cyano compounds are their high rotational viscosity (e.g., $\gamma_1 = 295\text{ mPa s}$ for the 4-cyano-4'-propylbicyclohexane, CCH-3) and their low voltage holding ratio (VHR less than 20 % of that of highly fluorinated materials), prohibiting their

application for AMD. As the reason for the high γ_1 of cyano compounds, intermolecular association phenomena^[4a] are discussed, caused by the "concentration" of the molecular dipole moment in one small but highly polar functional group.

For the design of new polar liquid crystals with lower rotational viscosity by reduced association, the overall dielectric anisotropy has therefore to be spread in small local dipoles over as large as possible part of the molecule.^[4b] In order to obtain representatives with very low birefringence, substructures without π -systems have to be incorporated into the liquid-crystal structure.

Based on this working hypothesis, we were interested in liquid crystals containing neither polar aromatic rings (such as unidirectionally connected pyrimidines, pyridines, or fluorinated benzene derivatives) nor the aliphatic low birefringent but unpolar cyclohexane ring (such as, e.g., CCH-33, 1). The structural element we selected to integrate several local dipoles directly into the mesogenic core of a low birefringence liquid crystal is the *trans*-1,3-dioxane building block.^[5,6]

AM1 calculations^[7] indicated that the combination of two dioxanes would result in a similar dielectric anisotropy as for cyanobicyclohexanes (e.g., $\Delta\epsilon = 9.4$ for CCH-3). Extension of this concept to tris(dioxane)s^[8] (5) was expected to produce even higher values for $\Delta\epsilon$ together with a very low birefringence.



Recent studies on novel liquid crystals for AMD applications identified the terminal difluorovinyl and difluorovinylmethoxy structures as especially promising with regard to mesogenic and viscoelastic properties. Yet, the resulting $\Delta\epsilon$ of purely carbocyclic compounds of type 6^[6a] ($\Delta\epsilon = 5.1$) or 8^[6c] ($\Delta\epsilon = -0.3$; for details see Table 1) is too small for our purpose. AM1 calculations predicted that the influence of the difluorovinyl(methoxy) group on the overall $\Delta\epsilon$ should be dramatically enhanced by combination with one or more *trans*-1,3-dioxane^[6c] substructures in the mesogenic core. The dielectric anisotropies of the structural hybrids 7 and 9–11 were expected to be much higher than those of the simple *trans*-1,3-dioxane derivatives 2–4 as well as 6 or 8. Owing to the wider distribution of the dipole moments in these compounds, the viscoelastic properties of 4,

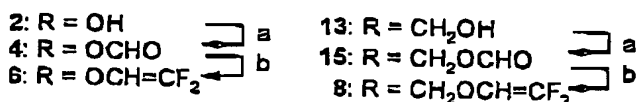
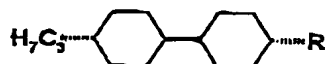
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7, and 9–11 are expected to be improved significantly compared with conventional substances with similar electro-optic characteristics such as, for example, the cyanobicyclohexanes.

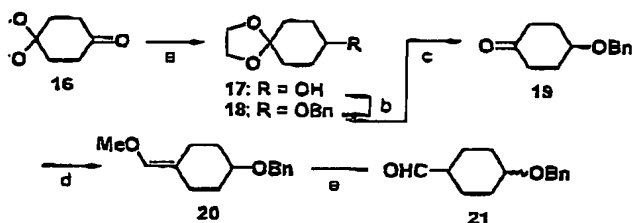
In order to verify the validity of this concept, the liquid crystals 2–9 as well as various homologues of 4 were synthesized and characterized with respect to their performance as polar and low birefringent components of LC mixtures.

The difluorovinyl ethers 6 and 8 were synthesized in two steps from the corresponding alcohols 12 and 13 (Scheme 1). These were converted into their formates 14 and 15, which were treated with CF_2Br_2 and $\text{P}(\text{NMe}_2)_3$ in a mixture of THF and dioxane (10:1)^[9] to furnish the target molecules 6 and 8.

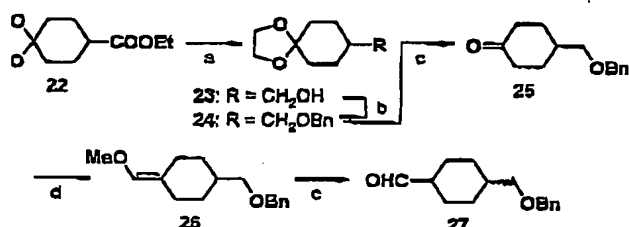


Scheme 1. Syntheses of the bicyclohexane derivatives 6 and 8: a) HCOOH , CCl_4 , THF; 0 °C → room temp., 4 h (14: 74 %, 15: 45 %). b) CF_2Br_2 , $\text{P}(\text{NMe}_2)_3$, THF/dioxane (10:1); 0 °C → room temp., 18 h (6: 42 %, 8: 40 %).

For the synthesis of compounds 7 and 10 first the building blocks 21 (Scheme 2) and 27 (Scheme 3) had to be prepared: Cyclohexanedione monoethylene ketal (16) was reduced to the alcohol 17, which was benzylated and saponi-



Scheme 2. Synthesis of the aldehyde building block 21: a) NaBH_4 , PrOH ; room temp., 18 h (97 %). b) 1. NaH , THF; 40 °C → 65 °C, 3 h; 2. BnBr , 65 °C, 18 h (76 %). c) HCOOH , toluene; room temp., 18 h (95 %). d) $\text{MeOCH}_2\text{PPh}_3^+\text{Br}^-$, KO^tBu , THF; -10 °C → room temp., 2 h (quant., side product). e) HCl , toluene (65 %, contains 90 % *trans*).

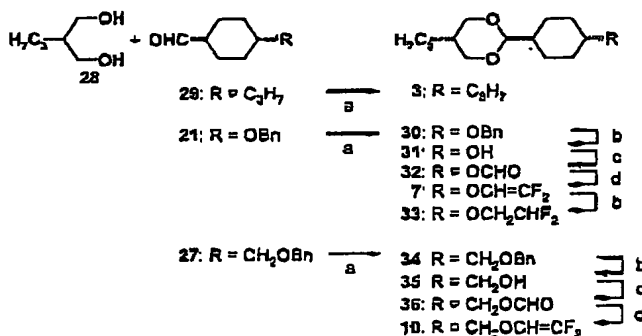


Scheme 3. Synthesis of the aldehyde building block 27: a) LiAlH_4 , THF; room temp., 3 h (quant., crude product). b) 1. NaH , THF; 40 °C → 65 °C, 3 h; 2. BnBr , 65 °C, 18 h (88 %). c) HCOOH , toluene; room temp., 18 h (84 %). d) $\text{MeOCH}_2\text{PPh}_3^+\text{Br}^-$, KO^tBu , THF; -10 °C → room temp., 2 h (87 %). e) HCOOH , toluene; room temp., 18 h (97 %).

fied to the ketone 19. A Wittig reaction with methoxymethyl triphenylphosphonium bromide yielded the enol ether 20, which was hydrolyzed to the aldehyde 21. Crystallization of crude 21 from *n*-heptane afforded the pure *cis* isomer. The desired *trans*-21 was enriched to about 90 % in the mother liquor, which was evaporated to dryness and used for the following reactions.

Building block 27 was prepared in a similar way from the alcohol 23, which is available from ester ketal 22 by reduction with LiAlH_4 in THF (see Scheme 3). Since neither of the isomers of the aldehyde 27 crystallized, the *cis*-*trans* mixture was used without prior separation for the subsequent ketalization step.

The building blocks 21 and 27 were condensed with the diol 28 to furnish the ketals 30 and 34 (Scheme 4). The benzyl protecting groups were removed by catalytic hydrogenation. The resulting alcohols were formylated to 32 and 36. Unfortunately, only 32 could be obtained as the pure *trans* isomer by crystallization from *n*-heptane. It was converted to the difluorovinyl ether 7 as already described for the syntheses of 6 and 8. Since the difluorovinyl ether 7 started to decompose through HF loss on extended storage at room temperature, a sample was hydrogenated to the stable compound 33.

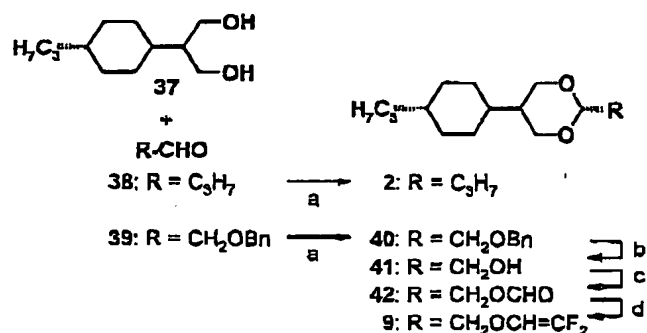


Scheme 4. Syntheses of the 4-propyl-2,6-dioxabicyclohexane derivatives 3, 7, 33, and 10: a) cat. $p\text{-TsOH}$, toluene; azeotropic removal of water (3: 34 %, 30: 25 %, 34: 37 %). b) H_2 , 5 % Pd-C , THF (31: 89 %, 35: 85 %, 33: 41 %). c) HCOOH , DCC , THF; 0 °C → room temp., 4 h (32: 70 %, 36: 15 %). d) CF_2Br_2 , $\text{P}(\text{NMe}_2)_3$, THF/dioxane (10:1); 0 °C → room temp., 18 h (7: 43 %, 10: complex mixture).

It was not possible to separate the *cis*-*trans* mixture of the formate 36 by the usual crystallization procedure. Furthermore, all attempts to obtain the difluorovinyl oxymethyl compound 10 from the formate isomeric mixture 36 failed.

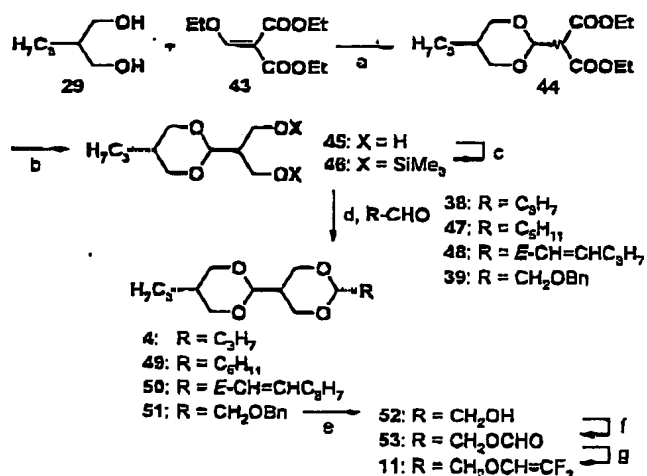
Compound 3 was prepared by acid-catalyzed condensation of 28 with aldehyde 29 (Scheme 4). The pure *trans*-*trans* isomer was obtained by crystallization from ethanol.

Acid-catalyzed condensation of the diol 37^[10] with the aldehydes 38 or 39 afforded compounds 2 and 40, respectively (Scheme 5). In both cases the pure *trans*-*trans* isomer was isolated by crystallization from ethanol. The benzyl ether 40 was converted to compound 9 in three steps (hydrogenation, formylation, modified Wittig reaction) in a similar way to that already described for 7.



Scheme 5. Syntheses of the 4-propyl-3',5'-dioxabicyclohexane derivatives 2 and 9: a) cat. *p*-TsOH, toluene; azeotropic removal of water (2: 27 %, 40: 47 %). b) H₂, 5 % Pd-C, THF (96 %). c) HCOOH, DCC, THF; 0 °C → room temp., 4 h (96 %). d) CF₂Br₂, P(NMe₂)₃, THF/dioxane (10:1); 0 °C → room temp., 18 h (14 %).

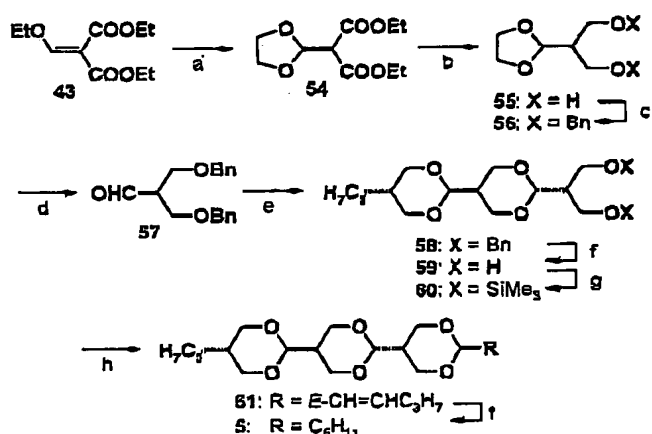
The key building block for the bis(dioxane)s 4 and 11 is the *trans*-diol 45.^[5] Since this compound contains a hidden bifunctionality (diol and ketal), all attempts at acid-catalyzed ketalization as described for the other ketals resulted in a complex mixture of polymeric products. The ketalization method developed by Noyori et al.^[11] offered an elegant alternative. The diol was converted to its bis(trimethylsilyl) ether 46 (Scheme 6). This was condensed with the aldehydes 38, 47, 48, and 39 under strictly aprotic conditions (cat. Me₃SiOTf, CH₂Cl₂; -78 °C) to furnish the ketals 4, 49, 50, and 51, respectively, in good yields with a *cis/trans* ratio of about 1:1.^[8] The pure *trans-trans* bis(dioxane)s 4, 49, and 50 were isolated by crystallization from *n*-heptane.



Scheme 6. Syntheses of the 4-propyl-2,6,3',5'-tetraoxabicyclohexane derivatives 4, 49, 50, and 11: a) cat. *p*-TsOH, xylene; distillative removal of EtOH (53 %). b) LiAlH₄, THF, reflux, 3 h (29 %). c) Me₃SiCl, DMF, NEt₃; 0 °C → room temp., 18 h (90 %). d) cat. Me₃SiOTf, CH₂Cl₂; -78 °C, 30 min (4: 21 %, 49: 39 %, 50: 32 %, 51 [cis/trans mixture]: 31 %). e) H₂, 5 % Pd-C, THF (65 %). f) HCOOH, DCC, THF; 0 °C → room temp., 4 h (20 %, pure *trans*). g) CF₂Br₂, P(NMe₂)₃, THF/dioxane (10:1); 0 °C → room temp., 18 h (complex mixture).

Since repeated crystallization of the benzylic ether 51 from *n*-heptane did not change the isomeric ratio, the benzyl group was removed by catalytic hydrogenation. The resulting alcohol 52 was formylated to 53. Chromatography and subsequent crystallization from *n*-heptane afforded pure *trans-trans* 53. All attempts to convert the formate 53 to the difluorovinyl ether by the usual method (CF₂Br₂, P(NMe₂)₃, THF/dioxane [10:1]) resulted only in complex mixtures. The reason might be a partial transketalization induced by the P(NMe₂)₃/CF₂Br₂ reagent, resulting in polydioxanes or other polymers.

For the synthesis of the tris(dioxane) 5 the dibenzylated aldehyde-diol 56 was prepared in a similar way as the diol 45 (Scheme 7). After deketalization of 56 the aldehyde 57 was purified by crystallization of its bisulfite adduct. The bis(silyl ether) 46 was reacted with 57 by the Noyori method to yield a *cis/trans* mixture of 58. This compound was



Scheme 7. Synthesis of the tris(dioxane)s 61 and 5: a) Ethylene glycol, cat. *p*-TsOH, xylene; distillative removal of EtOH (69 %). b) LiAlH₄, THF, reflux, 3 h (54 %). c) 1. NaH, THF; 40 °C → 65 °C, 3 h; 2. BuBr; 65 °C, 18 h (51 %). d) 1. HCOOH, toluene; room temp., 18 h; 2. NaHSO₃, H₂O, crystallization; 3. K₂CO₃, H₂O (55 %). e) 46, cat. Me₃SiOTf, CH₂Cl₂; -78 °C, 30 min (91 % *cis/trans* mixture). f) H₂, 5 % Pd-C, THF (59: 17 % pure *trans*, 5: 50 %). g) Me₃SiCl, DMF, NEt₃; 0 °C → room temp., 18 h (86 %). h) (E)-Hexenal, cat. Me₃SiOTf, CH₂Cl₂; -78 °C, 30 min (65 % *trans*).

hydrogenated to the diol 59 from which the pure *trans* compound was isolated by crystallization from THF. The *trans*-diol 59 was silylated to 60. This key intermediate was reacted with (E)-hexenal (48) in the same way as described for the synthesis of 50. Recrystallization from THF yielded pure all-*trans*-61. Since the extremely low solubility of this compound is an obstacle to its physical characterization, 61 was hydrogenated to 5. Unfortunately, the solubility of 5 was even lower.

Table 1 gives a comparative overview of the physical properties of all the newly synthesized liquid crystals. With the exception of the mesophases the cited data are not the properties of the particular single liquid-crystalline compounds, but extrapolated data from a standard LC mixture.^[12] A typical LCD never contains one single liquid crystal, but always a mixture of ca. 10 to 15 components.

Table 1. Comparison of the mesophases, extrapolated clearing points ($T_{NI,extr}$), dielectric anisotropies ($\Delta\epsilon$), birefringences (Δn), and rotational viscosities (γ_1) of the newly synthesized liquid crystals. The structure of the mesogenic core is abbreviated as follows: C = *trans*-cyclohexane, D = *trans*-1,3-dioxane. The phase transition temperatures (C = crystalline; S_B = smectic B; I = isotropic phase) are given in °C, the values for the rotational viscosity γ_1 in mPa s. Numbers in brackets denote monotropic phase transitions. $T_{NI,extr}$, $\Delta\epsilon$, Δn , and γ_1 were extrapolated from the liquid-crystal mixture Merck ZLI-4792 [12]. The DDD derivatives were insoluble in ZLI-4792.

No.	Core	R ¹	R ²	Mesophases	$T_{NI,extr}$	$\Delta\epsilon$	Δn	γ_1
1	CC	C ₃ H ₇	C ₃ H ₇	C 65 S _B 83 I	69.4	-0.3	0.043	29
2	CD	C ₃ H ₇	C ₃ H ₇	C 22 S _B 73 I	27.6	2.5	0.055	79
3	DC	C ₃ H ₇	C ₃ H ₇	C 36 S _B (36) N 36.4 I	7.7	1.6	0.045	55
4	DD	C ₃ H ₇	C ₃ H ₇	C 82 S _B 125 I	-0.7	8.3	0.048	98
49	DD	C ₃ H ₇	C ₃ H ₁₁	C 77 S _B 117 I	18.3	6.9	0.032	133
50	DD	C ₃ H ₇	(<i>E</i>)-CH=CHC ₃ H ₇	C 82 S _B 118 I	12.8	7.9	0.062	-
8	CC	C ₃ H ₇	CH ₂ OCH=CF ₂	C 2 S _B 51 I	21.7	-0.3	0.051	-
9	CD	C ₃ H ₇	CH ₂ OCH=CF ₂	C 18 I	-52.3	7.7	0.057	84
6	CC	C ₃ H ₇	OCH=CF ₂	C 30 N (13.2) I	-5.9	5.1	0.063	39
7	DC	C ₃ H ₇	OCH=CF ₂	C 26 I (slow dec.)	-69.6	13.2	0.053	-
33	DC	C ₃ H ₇	OCH ₂ CHF ₂	C 37 I	-51.9	11.9	0.055	-
5	DDD	C ₃ H ₇	C ₃ H ₁₁	C 169 S _B 234 I	-	-	-	-
61	DDD	C ₃ H ₇	(<i>E</i>)-CH=CHC ₃ H ₇	C 227 S _B (189) I	-	-	-	-

Blending is the only method to achieve a broad nematic phase range and to adjust electro-optic and viscoelastic properties exactly to the specifications required for an optimal display performance. Some of the components commonly used in LCDs do not even display mesophases as pure substances. For this reason, especially the physical behavior of a single liquid crystal in a complex mixture is of importance for the application-oriented evaluation of new materials.

Generally isocyclic as well as oxanalogous bicyclohexanes have a strong tendency to form smectic B (S_B) phases. Of the bisalkyl compounds only 3 has very small nematic phase range, and 6 has a monotropic nematic phase. For the bis(dioxane)s (DD) all phase transitions are—compared to their carbocyclic analogues—shifted to higher temperatures. The replacement of cyclohexane by dioxane building blocks lowers the extrapolated clearing points dramatically. Especially the exchange of the first ring seems to cause a big drop in the extrapolated clearing temperature: For the three pairs 1/3, 6/7, and 8/9 the difference is 60–70 K. 49 and 50 have the highest extrapolated clearing points in the bis(dioxane) series, both with side chains of a different length. The unusually large discrepancy between observed S_B–I transitions and the N–I transition temperature ($T_{NI,extr}$) extrapolated from ZLI-4792 is also remarkable. Especially in the series CC–CD–DC–DD (C = *trans*-cyclohexane, D = *trans*-1,3-dioxane) there seems to be no correlation between these data. Since the tris(dioxane)s 5 and 61 are both insoluble in the host mixture, no extrapolated data, such as $\Delta\epsilon$, could be determined. Both compounds have melting points above 200 °C and the same tendency to form S_B mesophases as the bis(dioxane)s.

The birefringence of all compounds ($\Delta n = 0.032$ – 0.055) is very low compared to fluorinated phenylcyclohexanes (typically $\Delta n \sim 0.075$) or even cyanobicyclohexanes ($\Delta n \sim 0.060$). Exchange of one alkyl side chain by pentenyl or di-

fluorovinylxy(methyl) leads to a slightly increased value for Δn (0.051–0.063), caused by the double bond.

Stepwise substitution of the *trans*-cyclohexane structure elements by *trans*-1,3-dioxane increases the dielectric anisotropy from the “neutral” bicyclohexane 1 over the low polar cyclohexyldioxanes 2 and 3 to the polar bis(dioxane)s 4, 49, and 50. The polarity of the bis(dioxane)s is in the same range as for cyanobicyclohexanes ($\Delta\epsilon \sim 8$ – 9). If the terminal alkyl group is replaced by a moderately polar difluorovinylxy or even an unpolar difluorovinylxymethyl function the polarity is enhanced dramatically.

The rotational viscosity of a LC single compound is one of the most important parameters owing to its influence on the switching time of the complex LC mixture that is used for the display application. In comparison with the similarly polar cyanobicyclohexanes ($\gamma_1 = 295$ mPa s for CCH-3) the γ_1 values of the DD homologues are about three times lower. This might be the result of the more homogeneous distribution of the dipole moments over the whole mesogenic core structure.

In contrast to all nitrile-containing liquid crystals (such as CCH-3), the voltage holding ratio of the bis(dioxane)s is in the same range as that of typical highly fluorinated materials. The DD compounds are therefore, among the strongly polar liquid crystals, the materials with the lowest birefringence that are still useful for application in active matrix displays.

The employment of Noyori's procedure^[11] for ketal formation under strictly aprotic conditions enabled us to synthesize and characterize a variety of new *trans*-1,3-dioxane based liquid crystals with alkyl as well as alkenyl side chains. Many of these compounds were up to now not accessible by the commonly used proton acid-catalyzed ketalization methods.^[5] It was also shown that, in contrast to all liquid crystals deriving their polarity from cyano groups, the bis(dioxane)s have no adverse effect on the voltage

holding ratio of TFT (thin film transistor) LC mixtures. For this reason and because of their low birefringence and favorable mesogenic properties, these new substances are quite attractive as a polar component of liquid-crystal mixtures for active matrix displays with shorter switching times and lower power consumption.

Received: October 30, 1997

Gelation of Room-Temperature Liquid Crystals by the Association of a *trans*-1,2-Bis(amino)cyclohexane Derivative**

By Takashi Kato,* Takaaki Kutsuna, Kenji Hanabusa, and Masakatsu Ukon

In recent years, the efficient gelation of organic solvents by low molecular weight compounds has attracted much attention.^[1-9] In several cases, hydrogen bonding is a key interaction for the fibrous association and the microphase separation of gelling agents in common organic solvents.^[1,4,6-9] One of the authors reported that the aggregation of a *trans*-1,2-bis(acylamino)cyclohexane through intermolecular hydrogen bonds results in the efficient gelation of a variety of organic solvents.^[6] These gels have great potential as functional soft materials.^[3,4,9] On the other hand, thermotropic liquid crystals are dynamic anisotropic fluids that have been developed recently as advanced materials for electro-optical applications.^[10] For such applications, anisotropic chemical gels were fabricated by the dispersion of covalently crosslinked polymers in liquid crystals.^[11-13] However, low molecular weight compounds have not been used to prepare anisotropic gels. We considered that physical anisotropic gels, which are a new class of gels, would be obtained if thermotropic room-temperature liquid crystals were efficiently gelled through molecular self-assembly of low molecular weight compounds.

We report here the gelation of room-temperature nematic liquid crystals by self-aggregation of low molecular weight molecules through hydrogen bonding. *trans*-(1*R*,2*R*)-Bis(dodecanoylamino)cyclohexane, **1**, was selected as the gelling agent of liquid crystals.^[6] 4-Pentyl-4'-(cyano)biphenyl, **2**, (nematic: 24–35 °C) and 4-(methoxy)-benzylidene-4'-(butyl)aniline, **3**, (nematic: 22–47 °C) were used as room-temperature liquid crystals.

These mesomorphic compounds **2** and **3** were successfully gelled by compound **1**. Once the gel is formed on cooling, the test tube filled with the sample can be turned

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